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Epoxide Cleavage Reactions of 7α,8α- and 7β,8β-Epoxycholestanol Acetates

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In a search for an alternative synthetic route to 32-oxygenated sterol derivatives such as **5**, 7α,8α- and 7β,8β-epoxycholestanol acetate (**9** and **10**) were subjected to various conditions of epoxide cleavage. The *trans*-diaxial opening of the α-epoxide **9** with lithium/ethylamine gave the 7α-ol **11**, whereas the 8β-ol **12** was produced from the β-epoxide **10** on reduction with lithium aluminum hydride. However, the *trans*-diaxial 8β-halo(or hydroxy)-7α-ols were not obtained at all on treatment of the α-epoxide **9** with various mineral acids or BF_3-etherate in benzene. Under these conditions, the C-8 carbenium ion would be the intermediate, from which the 7-ketone **13** and a mixture of $\Delta^{6,8}$-, $\Delta^{7,9}$-, $\Delta^{7,14}$- and/or $\Delta^{8,14}$-diene compounds **16**, as well as $\Delta^{8(9)}$- and $\Delta^{8(14)}$-7α-ol **14** and **4a**, were produced. The latter allylic alcohol **4a**, a possible synthetic precursor of 32-oxygenated sterol was prepared in 63% yield when benzene was replaced with tetrahydrofuran in the BF_3-etherate-catalyzed reaction of the α-epoxide **9**.

Keywords——epoxide cleavage; 32-oxygenated sterol; 7α,8α-epoxycholestanol acetate; 7β,8β-epoxycholestanol acetate; 3β-acetoxycholest-8(14)-en-7α-ol; reduction; acid treatment; boron trifluoride-etherate; long-range ^{13}C–^{1}H COSY

The 32-oxygenated lanosterol derivatives have an important role as intermediates of cholesterol biosynthesis. However, there is essentially only one method available for their chemical preparation[1] (Chart 1). This is based on the Barton-Kalvoda reaction[2] of the 7α-hydroxylanostanol derivative **1**, followed by acidic cleavage of the resultant 7,32-epoxide **2** to yield an olefinic mixture of the Δ^6-, Δ^7- and Δ^8-32-alcohol. We have envisaged two possible alternative preparations of 32-oxygenated lanosterol derivatives such as **5**. One is *via* reductive cleavage of the bromoether **7** derivable from the 8β-bromo-7α-ol **6**, and the other rests on a cyclic rearrangement[3] of an appropriate derivative having the 7α-hydroxyl-8(14)-ene system **4b**. Both the requisite bromohydrin **6** and the allylic alcohol **4** would be available by proper cleavage of the 7α,8α-epoxide (**3a** or **3b**). With these considerations in mind, 7α,8α- and 7β,8β-epoxycholestanyl acetates (**9** and **10**) have now been subjected to reactions under reductive and acidic or basic conditions.

The 7α,8α-epoxide **9** and the 7β,8β-epoxide **10** (17 : 1) were prepared by oxidation of the Δ^7-olefin **8** with *m*-chloroperbenzoic acid.[4] In accord with the previous observations,[1b,c,5] the α-epoxide **9** on treatment with lithium in ethylamine in the presence of *tert*-butanol yielded the 3β,7α-diol **11** and Δ^7-olefin **8** (3-OH) in a 5 : 1 ratio as analyzed by gas chromatography-mass spectrometry (GC-MS). On the other hand, this epoxide was resistant to reduction with lithium aluminum hydride (LAH) in refluxing tetrahydrofuran (THF). The aluminum hydride anion is bulkier than an electron on metal and hence its β-face approach to C-8 would be prevented by the angular C-10 and C-13 methyl groups, whereas the less hindered equatorial (7β) attack, which should afford an 8α-OH steroid, would not occur because of the highly strained nature of the B/C *cis* ring system. In contrast, the β-epoxide **10** was almost quantitatively reduced with LAH to give the 3β,8β-diol **12**. The 8β-hydroxyl function of this

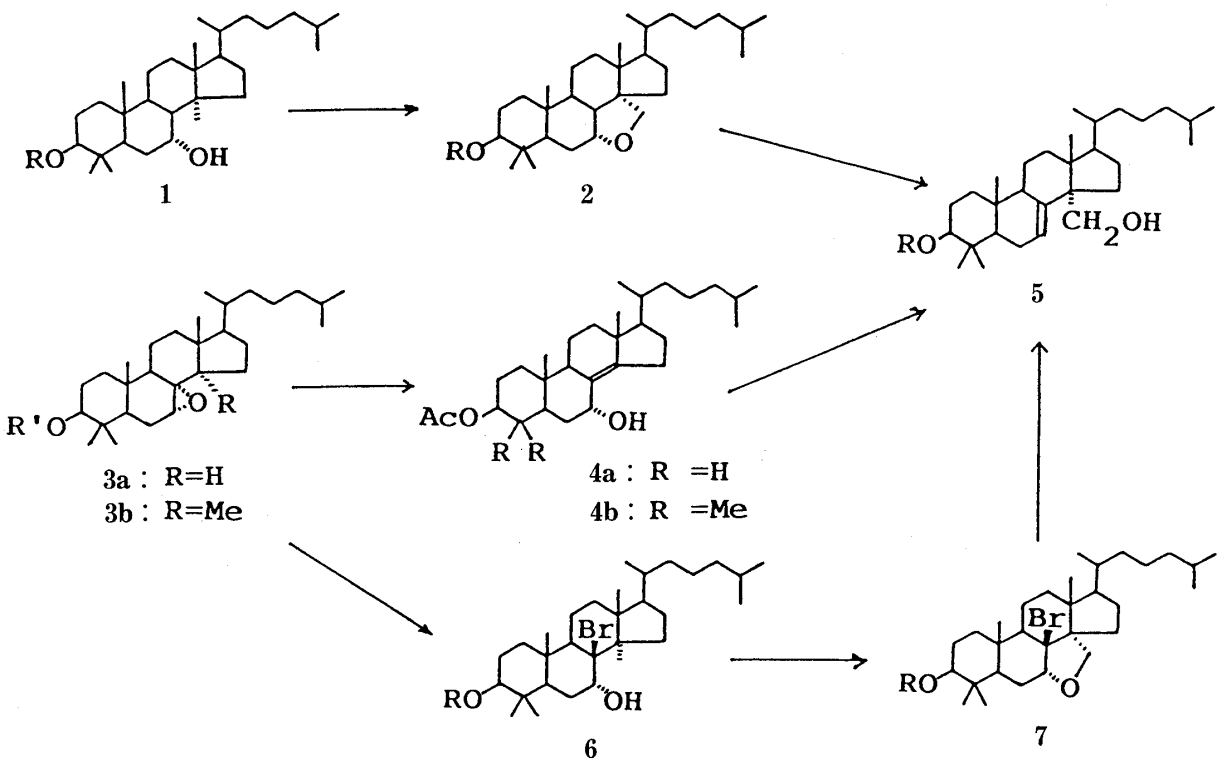
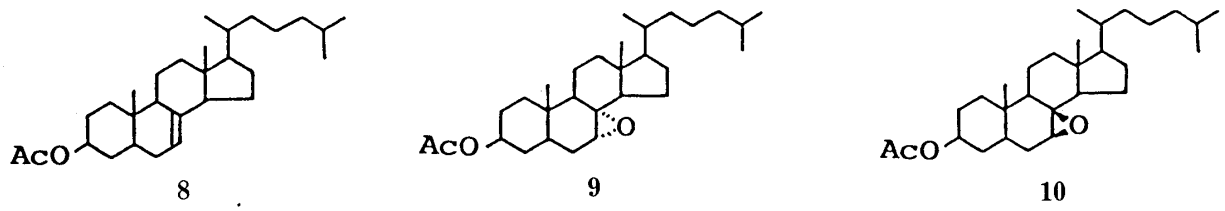
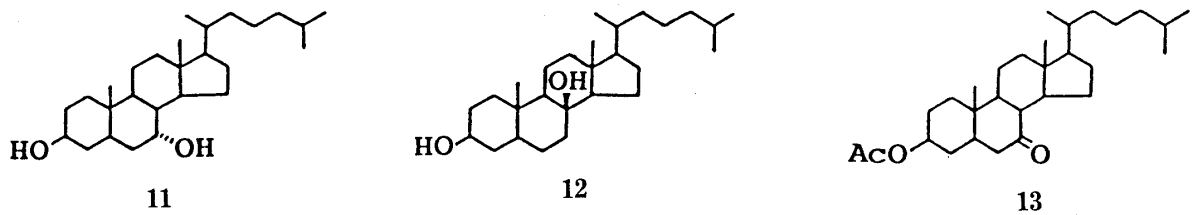


Chart 1





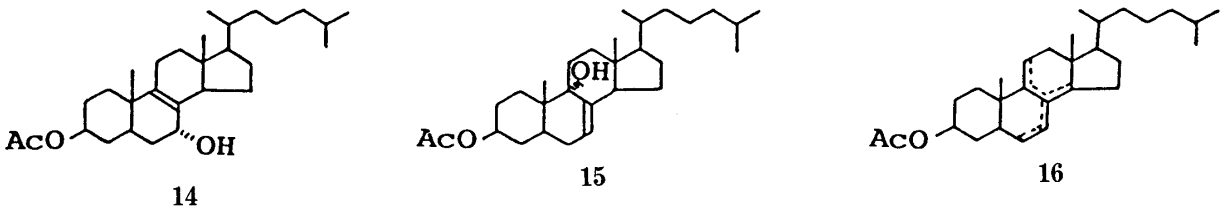


Chart 2

diol was deduced from its resistance to acetylation and also from the nuclear magnetic resonance (NMR) data (Experimental), which showed downfield shifts of the 10- and 13-methyl groups which are located 1,3-diaxially positions to the 8β-hydroxyl group.[6)]

Interaction of an attacking nucleophile with angular methyl groups was also observed on acidic cleavage of the α-epoxide **9**. Thus, when this epoxide was treated with dilute sulfuric acid in $CHCl_3$,[7,8] perchloric acid in THF[8] or hydrobromic acid in $CHCl_3$, no vicinal glycol(7α,8β-diol) was produced. In the last case, the expected 7α-hydroxy-8β-bromide was not detected at all in the reaction products. Instead, the products were found to be a mixture of the conjugated dienes **16**, the 7-ketone **13**,[9] and/or the allylic alcohols **4a** and **14**. The dienes **16** were identified by NMR and high-performance liquid chromatographic (HPLC) analysis with the aid of authentic samples of $\Delta^{6,8}$-, $\Delta^{7,9}$-, $\Delta^{7,14}$- and $\Delta^{8,14}$-cholestadienol acetate.[10] Structural assignments of **4a** and **14** were based on ^{1}H-NMR analysis (Experimental), and also on their transformation into the separable mixtures of 8α,9α- and 8α,14α-epoxycholestanol acetate,[4] whose ^{1}H-NMR spectra were consistent with the reported ones for 3-desacetoxy analogs.[11] All of these reaction products **4a**, **13**, **14** and **16** can be considered to be formed *via* the C-8 carbenium ion.

Similarly, reaction of the α-epoxide **9** with BF_3-etherate in benzene[12] afforded the diene mixture **16** and the 7-ketone **13** in 72% and 13% yields, respectively, whereas the β-epoxide afforded the diene mixture **16** and the 7-ketone **13** in 58% and 22% yields, respectively. Although hydride shift in the β-epoxide **10** could yield a 7-ketone with 8α-H configuration, the actual product was the same 8β-H ketone **13** as obtained from the α-epoxide **9**. This result and the formation of the diene mixture **16**, again suggest intermediacy of the C-8 carbenium ion. To our gratification, 7α-hydroxyl-8(14)-ene **4a**, which is a candidate as a synthetic precursor for 32-oxygenated sterols, became the predominant product when benzene was replaced with THF in this BF_3-catalyzed rearrangement reaction. Thus, NMR analysis of the allylic alcohol fraction indicated that **4a** and **14** were produced in 63% and 13% yields, respectively. Isolation of **4a** (29% yield) was effected by recrystallization. In addition to **4a** and **14**, the third allylic alcohol 9α-hydroxyl-7-ene **15** (4% yield) was also isolated from the reaction products. The assigned structure of **15** is consistent with the ^{1}H-NMR signals of 7-H at 5.26 ppm and of the 10- and 13-methyl groups which are within 0.05 ppm of the calculated values.[13] Further, a cross peak between the 10-methyl protons and an oxygenated tertiary carbon (C-9) was observed (Experimental) in a (C, H) correlation spectroscopy (COSY) spectrum enhancing long-range couplings[14] of the corresponding 3-methoxymethyl ether derivative.[15] Further support came from the acid-catalyzed dehydration of **15** to yield the 7,9(11)-diene as a major product.

Finally, in the expectation of a more selective formation of the 7α-hydroxyl-8(14)-ene **4a**, the α-epoxide **9** was treated with lithium diethylamide, diisopropylamide, and diisobutylamide in THF,[16] but the only observed reaction was hydrolysis of the acetyl group, leaving the epoxide moiety intact.

Experimental

Melting points were measured on a micro melting point apparatus (Yanaco) and are uncorrected. NMR spectra were taken with a JEOL JMN-GX270 spectrometer for solutions in deuteriochloroform and are reported in δ. ^{1}H-NMR spectra (270 MHz) are referenced to internal tetramethylsilane at 0.00 ppm and ^{13}C-NMR spectra (68 MHz) are referenced to the center of the solvent triplet at δ 77.00 ppm. Gas liquid chromatographic analyses (GC) were performed on a Shimadzu GC-8A using a 1.5% OV-17 column (1 m) at 240 °C. HPLC were performed on a Shimadzu LC-5A using a Zorbax ODS column (4.6 mm i.d. × 15 cm; detector setting, UV 210 nm) with methanol as the solvent at a flow rate of 1.0 ml/min. MS were taken with a JEOL JMS-DX303 using a direct inlet system or a GC-MS system using an Ultra Performance capillary column (0.17 μ thickness, 0.31 mm i.d. × 25 m) at 260 °C with a 1/60 split. Column chromatography was performed with Kieselgel 60 (Merck, 70—230 mesh). Thin layer chromatography (TLC) was carried out on precoated Kieselgel 60 F_{254} plates (Merck, 0.25 mm thick). The usual work-up refers to dilution with brine, extraction and evaporation of the extract under vacuum. The samples (*ca.* 0.5 mg) to be analyzed by GC were derivatized to trimethylsilyl (TMS) ethers by heating with trimethylsilylimidazole (50 μl) in a sealed tube at 80 °C for 1 min and a 1-μl portion of the resultant solution was injected into the GC column.

Preparation of 3β-Acetoxycholest-7-ene (8)——A solution of 7-dehydrocholesterol (8.0 g, Aldrich) in a mixture of ethanol (400 ml) and dioxane (250 ml) was stirred with Raney Ni-W4 (*ca.* 4 g) under hydrogen at room temperature for 16 h. The catalyst was filtered off and the solvents were removed by evaporation. The residue showed two peaks (1 : 5) on HPLC at retention times of 12.0 min (cholest-8(14)-en-3β-ol) and 13.7 min (cholest-7-en-3β-ol). The crude products were treated with a mixture of acetic anhydride (25 ml) and pyridine (50 ml) to give a mixture of the acetates (7.9 g), which was recrystallized from methanol and dichloromethane to give 3β-acetoxycholest-7-ene (**8**), 5.25 g, mp 116—117 °C (ref. 9 mp 118—119 °C), ^{1}H-NMR δ: 0.54 (3H, s, 13-Me), 0.81 (3H, s, 10-Me), 0.86, 0.87 (each 3H, d, J=6.6 Hz, 25-Me_2), 0.92 (3H, d, J=6.6 Hz, 20-Me), 4.70 (1H, m, 3-H), 5.15 (1H, m, 7-H).

Preparation of the 7,8-Epoxides (9 and 10)——The 7-ene (**8**) (5.0 g) was dissolved in dichloromethane (100 ml), and $NaHCO_3$ (2.8 g) was added,followed by *m*-chloroperbenzoic acid (2.8 g). The mixture was stirred at room temperature for 2 h, and then the whole was diluted with dichloromethane, washed with 5% NaOH and brine, dried and evaporated to give an oil. This was chromatographed on silica gel with *n*-hexane–ethyl acetate (40 : 1—30 : 1) to give the β-epoxide (**10**) (0.19 g), mp 101—102 °C (from *n*-hexane–acetone), ^{1}H-NMR δ: 0.82 (3H, s, 13-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me_2), 0.91 (3H, s, 10-Me), 0.91 (3H, d, J=6.6 Hz, 20-Me), 2.01 (3H, s, 3-OAc), 2.80 (1H, d, J=5.3 Hz, 7-H), 4.63 (1H, m, 3-H), high-resolution MS *m/z*: Calcd for $C_{29}H_{48}O_3$: 444.3604; Found: 444.3603 (M^+), and the α-epoxide (**9**), (3.3 g), mp 95—97 °C (from *n*-hexane–acetone), ^{1}H-NMR δ: 0.71 (3H, s, 13-Me), 0.84 (3H, s, 10-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me_2), 0.92 (3H, d, J=6.6 Hz, 20-Me), 2.01 (3H, s, 3-OAc), 3.29 (1H, m, 7-H), 4.64 (1H, m, 3-H), high-resolution MS *m/z*: Calcd for $C_{29}H_{48}O_3$: 444.3604; Found: 444.3610 (M^+).

Reduction of the α-Epoxide 9 with Lithium/Ethylamine——Lithium (30 mg) was added to a mixture of the α-epoxide (**9**) (50 mg) and ethylamine (5 ml), and the mixture was stirred under nitrogen at −78 °C for 10 min, at −16 °C for 1 h, at 0 °C for 1.5 h and at room temperature for 16 h. Usual work-up using dichloromethane for extraction gave a solid residue (43 mg). This was treated with 5% KOH–methanol (3 ml) at room temperature for 2 h and at 40 °C for 15 min. Usual work-up using ethyl acetate for extraction gave a solid residue (40 mg). A part of this material (*ca.* 0.5 mg) was derivatized to the TMS ether and an aliquot was analyzed by GC and GC-MS. Four peaks (15 : 3 : 2 : 1) were found on GC (260 °C) at 8.0 min (3β,7β-diol bis-TMS ether), 8.7 min (cholest-7-ene-3β-ol TMS ether), 10.9 min (*m/z* 458, 429, 353, 143, unidentified) and 11.3 min (unidentified). No peak appeared at 8.1 min due to cholest-8-en-3β-ol TMS ether.

Treatment of the α-Epoxide 9 with LAH——A solution of the α-epoxide (**9**) (30 mg) in tetrahydrofuran (1 ml) was refluxed with LAH (27 mg) for 5 h. The usual work-up using ethyl acetate for extraction gave a 7α,8α-epoxycholestan-3β-ol (27 mg), mp 140—142 °C (from methanol), ^{1}H-NMR δ: 0.71 (3H, s, 13-Me), 0.82 (3H, s, 10-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me_2), 0.92 (3H, d, J=6.6 Hz, 20-Me), 3.30 (1H, m, 7-H), 3.55 (1H, m, 3-H), high-resolution MS *m/z*: Calcd for $C_{27}H_{46}O_2$: 402.3498; Found: 402.3501 (M^+), which comigrated on TLC with authentic 7α,8α-epoxycholestan-3β-ol prepared by oxidation of cholest-7-en-3β-ol with *m*-chloroperbenzoic acid.

Reduction of the β-Epoxide 10 with LAH——A solution of the β-epoxide (**10**) (50 mg) in tetrahydrofuran (1.5 ml) was stirred with LAH (20 mg) for 2 h. The ^{1}H-NMR spectrum of the reaction product indicated that the acetoxyl group had been converted to a hydroxyl group without affecting the epoxide moiety. The crude product was refluxed with LAH (20 mg) in THF (2 ml) for 5 h. Usual work-up gave an amorphous material (46 mg), and crystallization from methanol gave cholestane-3β,8β-diol (**12**), mp 141—146 °C, ^{1}H-NMR δ: 0.92 (3H, s, 13-Me), 0.97 (3H, s, 10-Me), 3.60 (1H, m, 3-H), ^{13}C-NMR δ: 71.4 (C3), 74.5 (C8), high-resolution MS *m/z*: Calcd for $C_{27}H_{48}O_2$: 404.3654; Found: 404.3625 (M^+).

Reaction of the α-Epoxide 9 with Mineral Acids——1) Treatment with Dilute Sulfuric Acid: Chloroform (5 ml) was shaken with 30% sulfuric acid (3 ml) and the organic solvent was separated and dried over magnesium sulfate. The α-epoxide (**9**) (10 mg) was dissolved in this acidic chloroform (0.25 ml) and allowed to stand at 60 °C for 4 h. Usual work-up and chromatography on silica gel gave a diene mixture (**16**) (0.8 mg), ^{1}H-NMR δ: 4.69 (m, 3-H), 5.35, 5.45 (each m, 7- and 11-H), 5.50, 5.73 (each m, 7- and 15-H). The intensity of these signals indicated that the mixture consisted of the 7,9-diene and 7,14-diene in a ratio of *ca.* 1 : 2. Further elution afforded the allylic alcohols (8 mg), ^{1}H-NMR δ: 0.59 (s, 13-Me of **14**), 0.69 (s, 13-Me of **4a**), 0.85 (s, 10-Me of **4a**), 0.94 (d, J=6.6 Hz, 20-Me of **4a**), 2.02 (s, 3-OAc), 4.00 (m, 7-H of **14**), 4.52 (m, 7-H of **4a**). The intensity of these signals indicated that the allylic alcohols consisted of **4a** and **14** in a ratio of *ca.* 2 : 1.

Acetylation of **4a** and **14**: The mixture of **4a** and **14** (168 mg) was treated with a mixture of acetic anhydride (1 ml) and pyridine (1 ml) at room temperature for 16 h. Usual work-up gave a solid residue, ^{1}H-NMR δ: 0.58 (s, 13-Me of **14**-acetate), 0.71 (s, 13-Me of **4a**-acetate), 2.02, 2.03, 2.04, 2.05 (each s, AcO), 4.73 (m, 3-H), 5.14 (m, 7-H of **14**-acetate), 5.58 (m, 7-H of **4a**-acetate).

Oxidation of **4a** and **14** with Pyridinium Chlorochromate: A suspension of pyridinium chlorochromate (55 mg) in dry dichloromethane (1 ml) was stirred at room temperature for 5 min. Then a solution of the mixture of **4a** and **14** (2 : 1, 19 mg) in dry dichloromethane (2 ml) was added, and the resultant mixture was stirred at room temperature for 10 min, then passed through a Florisil column with dichloromethane to give a diene mixture (**16**) (13 mg). The intensity of olefinic proton signals indicated that this mixture consisted of the 7,14- and 7,9-dienes in a ratio of *ca.* 2 : 1.

Oxidation of **4a** and **14** with *m*-Chloroperbenzoic Acid: *m*-Chloroperbenzoicacid (30 mg) was added a solution of

the mixture of **4a** and **14** (2 : 1, 63 mg) in dichloromethane (1.2 ml). The mixture was stirred at room temperature for 1.5 h and then diluted with dichloromethane. The whole was washed with 10% NaOH and brine, dried and evaporated to give solid residue (60 mg). This was chromatographed on silica gel with *n*-hexane–ethyl acetate (50 : 1—20 : 1) to give 3β-acetoxy-8,14-epoxycholestan-7α-ol (36 mg), mp 122—123 °C (from methanol), (ref. 9 mp 122—123 °C), ^{1}H-NMR δ: 0.87 (6H, d, J=6.6 Hz, 25-Me$_2$), 0.91 (3H, s, 13-Me), 0.92 (3H, s, 10-Me), 3.56 (1H, m, 7-H), 4.72 (1H, m, 3-H) and 3β-acetoxy-8,9-epoxycholestan-7α-ol[9] (17 mg), mp 149—150 °C, ^{1}H-NMR δ: 0.65 (3H, s, 13-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me$_2$), 1.12 (3H, s, 10-Me), 3.94 (1H, m, 7-H), 4.68 (1H, m, 3-H).

2) Treatment with Perchloric Acid: A mixture of the α-epoxide (**9**) (10 mg), THF (0.5 mg) and 30% $HClO_4$ (20 μl) was stirred at room temperature for 15 min. Usual work-up using ethyl acetate for extraction gave a solid residue (10 mg). Two peaks (1 : 1) were detected on HPLC at 13.4 min (the 7,14-diene) and 15.3 min (the 7,9-diene).

3) Treatment with Hydrobromic Acid: A mixture of the α-epoxide (**9**) (10 mg), chloroform (1 ml) and 47% hydrobromic acid (10 μl) was stirred at room temperature for 30 min. Usual work-up using chloroform for extraction gave a solid residue (10 mg). Two peaks were detected on HPLC at 13.4 min (the 8,14-diene) and 15.3 min (the 6,8- and 7,9-dienes), ^{1}H-NMR δ: 5.37 (m, 15-H of the 8,14-diene), 5.45 (m, 7- or 11-H of the 7,9-diene), 5.22, 6.12 (each m, 6- and 7-H of the 6,8(14)-diene). The intensity of the olefinic signals indicated that the reaction mixture consisted of the 8,14-, 7,9- and 6,8(14)-dienes in a ratio of *ca.* 8 : 1 : 1.

Treatment of the α-Epoxide 9 with BF_3-Etherate in Benzene——A mixture of the α-epoxide (**9**) (50 mg), benzene (2 ml) and BF_3-etherate (50 μl) was stirred at room temperature for 20 min. Usual work-up using ethyl acetate for extraction gave an oil (52 mg). This was chromatographed on silica gel with *n*-hexane–ethyl acetate (5 : 1) to give the 7-ketone (**13**), 6.5 mg, 13%, mp 149—150 °C (ref. 9 mp 148—149.5 °C), ^{1}H-NMR δ: 0.65 (3H, s, 13-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me$_2$), 0.91 (3H, d, J=6.6 Hz, 20-Me), 1.09 (3H, s, 10-Me), 2.02 (3H, s, 3-OAc), 4.68 (1H, m, 3-H), MS *m/z*: 444 (M^+), 426, 411 and a mixture of dienes (**16**) (36 mg, 72%). The ^{1}H-NMR spectrum of the diene mixture in the region of 5.0—6.3 ppm indicated that this was a mixture of the 6,8(14)-, 7,9-, 7,14- and 8,14-dienes in a ratio of *ca.* 15 : 1 : 2 : 4.

Treatment of the β-Epoxide 10 with BF_3-Etherate in Benzene——A mixture of the β-epoxide (**10**) (50 mg), benzene (2 ml) and BF_3-etherate (50 μl) was stirred at room temperature for 20 min. Usual work-up using ethyl acetate for extraction gave solid residue (49 mg) which was chromatographed on silica gel to give the 7-ketone (**13**) (11 mg, 22%),[9] and a mixture of the 6,8(14)-, 7,9-, 7,14- and 8,14-dienes (**16**) (29 mg, 58%) in a ratio of *ca.* 10 : 10 : 5 : 7.

Treatment of the α-Epoxide 9 with BF_3-Etherate in THF——A mixture of the α-epoxide (**9**) (120 mg), THF (4 ml) and BF_3-etherate (50 μl) was stirred at −15 °C under argon for 5 min. Usual work-up using ethyl acetate for extraction gave an oil (129 mg). This was chromatographed on silica gel to give a 1 : 1 mixture of the 7,9- and 7,14-dienes (**16**) (19 mg, 16%), a mixture (91 mg, 76%) of the 8(14)-en-7α-ol (**4a**) and the 8(9)-en-7α-ol (**14**) (5 : 1), which was recrystallized from methanol to give **4a** (34 mg), high-resolution MS *m/z*: Calcd for $C_{29}H_{48}O_3$: 444.3604; Found: 444.3592 (M^+) and the 7-en-9α-ol (**15**) (5 mg, 4%), mp 174—175 °C (from methanol), ^{1}H-NMR δ: 0.55 (3H, s, 13-Me), 0.86 (6H, d, J=6.6 Hz, 25-Me$_2$), 0.91 (3H, s, 10-Me), 2.02 (3H, s, 3-OAc), 4.68 (1H, m, 3-H), 5.25 (1H, m, 7-H), ^{13}C-NMR δ: 11.1 (C-18), 15.0 (C-19), 73.0 (C-3), 73.8 (C-9), 121.2 (C-7), 140.7 (C-8), high-resolution MS *m/z*: Calcd for $C_{29}H_{48}O_3$: 444.3604; Found: 444.3617 (M^+). The long-range ^{13}C–^{1}H COSY spectrum of 15 (3-methoxymethyl ether)[15] was obtained as follows. The values of the delays τ_1 and τ_2 were set at 62.5 and 31.3 ms, respectively. The spectral widths were 1530.0 Hz in f_1 and 15015.0 Hz in f_2 with a 128 × 1024 data-point matrix. The transform size was 256 × 2048 with zero filling. Data were handled in the power with the exponential window in both dimensions. The sample concentration was 0.3 M in deuterochloroform. The following cross peaks were observed: from 18-H (0.55 ppm) to C-12 (36.0 ppm), C-13 (43.5 ppm), C-14 (51.0 ppm) and C-17 (55.9 ppm); from 19-H (0.90 ppm) to C-1 (29.4 ppm) C-5 (33.0 ppm) C-10 (38.9 ppm) and C-9 (73.7 ppm).

Treatment of the α-Epoxide 9 with Base——A 15% *n*-butyl lithium–*n*-hexane solution (150 μl) was added to a solution of the dialkylamine (0.5 mmol) in anhydrous ether (1 ml), and the mixture was stirred under argon at room temperature for 15 min. A solution of the α-epoxide (**9**) (39 mg) in anhydrous ether (1 ml) was then added, and the mixture was refluxed for 4 h. Usual work-up using ethyl acetate for extraction gave an amorphous material which comigrated on TLC with authentic 7α,8α-epoxycholestan-3β-ol.

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	HPLC r.t. (min)	λ_{max} (nm)	Chemical shift (ppm) 10-Me	13-Me	Olefinic-H	
$\Delta^{6,8}$	15.3	244 (s), 251, 259 (s)	0.89	0.66	5.22	6.12
$\Delta^{7,9}$	15.3	235 (s), 243, 250 (s)	0.91	0.50	5.35	5.45
$\Delta^{7,14}$	13.4	243	0.83	0.80	5.50	5.73
$\Delta^{8,14}$	13.4	250	1.00	0.81	5.37	

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